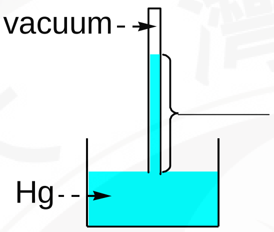
5 Gases

1643 Torricelli (1608-1647) designed barometer



760 mmHg
= 1 atm ~ 1 bar
= 14.7 lb/in^2
(psi)

(1 mmHg = 1 Torr)

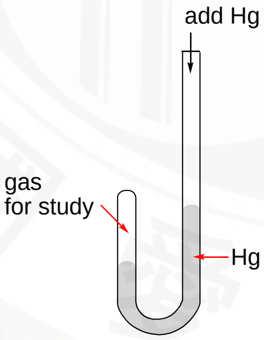
1 bar = 10^5 Pa
= 10^5 N/m^2

1 atm
= 1.01325×10^5 pa

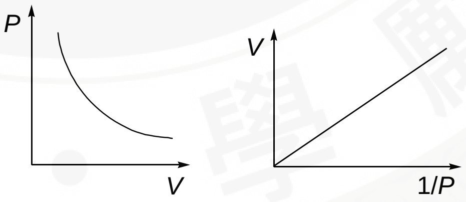
1654 Guericke (1602-1686) invented vacuum pump

※ The Gas Laws

◎ Boyl's law (1627 – 1691)

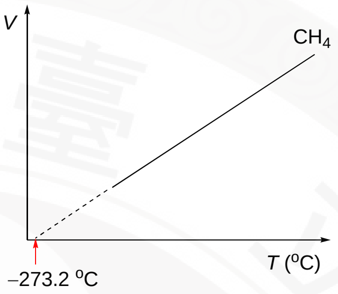


$PV = k$ ← A constant



◎ Charles's law (1746 – 1823)

1787 At constant P
(1802 also by Gay-Lussac)
$V \propto$ temperature



Kelvin temperature scale
T (in K) = t (in °C) + 273 ⇨ $V = bT$

◎ Avogadro's law
(explain Gay-Lussac's law of combining volumes)

$V = an$

Number of moles

※ The ideal gas law

Avogadro's law	$V \propto n$ (n: number of particles)
Boyle's law	$V \propto 1/P$ (P: pressure)
Charles's law	$V \propto T$ (T: temperature in K)

Combined form: $$V = R\left(\frac{Tn}{P}\right)$$

Universal gas constant: 0.08206 L·atm·K^{-1}·mol^{-1}

⇨ Ideal gas law $PV = nRT$

At STP (0 °C, 1 atm)
V = 22.42 L for 1 mol of gas

Molar volume

Application

Density $d = \frac{m}{V}$

$$m = dV = \frac{dnRT}{P}$$

molar mass $= \frac{dRT}{P}$ (mass with n = 1 mol)

Knowing d of a gas at a given T and P

⇨ Molar mass can be calculated

※ Dalton's law of partial pressures

(1803)

$$P_{total} = P_1 + P_2 + P_3 + \bullet\bullet\bullet$$

$$= \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + \bullet\bullet\bullet$$

$$= (n_1 + n_2 + n_3 + \bullet\bullet\bullet)\frac{RT}{V} = n_{total}\frac{RT}{V}$$

Mole fraction $X_1 = \frac{n_1}{n_{total}} = \frac{P_1}{P_T}$

⇨ $P_1 = X_1P_T$

※ The kinetic molecular theory of gases

Ideal gas law – Determined from experiments
Can be used for prediction
Does not tell why

To understand why
Build a theory (a model) { Simple
Complex

◎ A simple model of an ideal gas

- ✓ Particles are very small
  - V of particles can be neglected
  - Inter-particle distance is large: diffusibility
    compressibility
- ✓ In constant motion
  - Exert pressure on the walls
  - Fact: very light gas can exert high pressure
    → collide the walls in high frequency and velocity
  - Also explains diffusion
- ✓ No inter-particle forces: elastic collision
  - No lost of pressure

✓ Average KE ∝ *T* (in K)

Mixing of two different gases at the same T
→ no change of average KE
Also explains Dalton's law

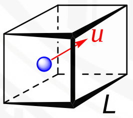
✓ Qualitative agreement with ideal gas law

constant T: V ↑ → P ↓
constant V: T ↑ → P ↑

※ Quantitative treatment

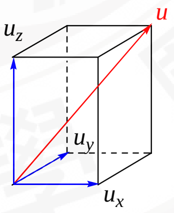
1857 Clausius (1822 – 1857)

Particle in a box with a velocity u



Velocity components on *x, y, and z* axis:
u_x, u_y, and u_z

$$u^2 = u_x^2 + u_y^2 + u_z^2$$



$$(\text{collision frequency})_x = \frac{u_x}{L}$$

$$F_x = ma_x = m\frac{\Delta u_x}{\Delta t} = \frac{\Delta(mu_x)}{\Delta t}$$

Since $\Delta t = \dfrac{L}{u_x}$

$$F_x = \frac{\Delta(mu_x)}{\Delta t} = \frac{2mu_x}{L/u_x} = \frac{2mu_x^2}{L}$$

$$F_{\text{total}} = \frac{2mu_x^2}{L} + \frac{2mu_y^2}{L} + \frac{2mu_z^2}{L} = \frac{2mu^2}{L}$$

The average

$$\overline{F}_{\text{total}} = \frac{2m\overline{u^2}}{L}$$

($\overline{u^2}$: the avg. of the square of the velocity)

$$P = \frac{\overline{F}_{\text{total}}}{\text{Area}} = \frac{2m\overline{u^2}}{6L^3} = \frac{m\overline{u^2}}{3L^3} = \frac{m\overline{u^2}}{3V}$$

$6L^2$

For nN_A of particles

moles Avogadro's #

$$P = nN_A \frac{m\overline{u^2}}{3V}$$

Kinetic E per particle $= \dfrac{1}{2}m\overline{u^2}$ (1 J = 1 kg•m^2/s^2)

joule

$$P = nN_A \frac{m\overline{u^2}}{3V} = nN_A \frac{2}{2}\frac{m\overline{u^2}}{3V} = \frac{2}{3}\frac{nN_A(\frac{1}{2}m\overline{u^2})}{V}$$

Define $(\text{KE})_{\text{avg}}$ as average kinetic E for 1 mol of particles

$$P = \frac{2}{3}\frac{n(\text{KE})_{\text{avg}}}{V} \quad \text{or} \quad \frac{PV}{n} = \frac{2}{3}(\text{KE})_{\text{avg}}$$

Postulation: KE $\propto T$

⇨ $\frac{PV}{n} \propto T$ ← Derived from theory

From experiment: $\frac{PV}{n} = RT$

⇨ $\frac{PV}{n} = \frac{2}{3}(\text{KE})_{\text{avg}} = RT$ or $\boxed{(\text{KE})_{\text{avg}} = \frac{3}{2}RT}$

$(\text{KE})_{\text{avg}} = N_{\text{A}}(\frac{1}{2}m\overline{u^2}) = \frac{3}{2}RT$

⇨ $N_{\text{A}}m\overline{u^2} = 3RT$ ⇨ $\overline{u^2} = \frac{3RT}{M}$ (M: molecular weight)

Qualitatively: M ↑ ⇨ $\overline{u^2}$ ↓

$\sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$

|||

u_{rms} : root mean square velocity

R = 8.3145 J·K^{-1}mol^{-1} = 8.3145 kg·m^2·s^{-2}·K^{-1}mol^{-1}

For O_2 at STP: u_{rms} ~ 500 m/s
However, mean free path = 1 × 10^{-7} m at STP
(the distance between collisions)

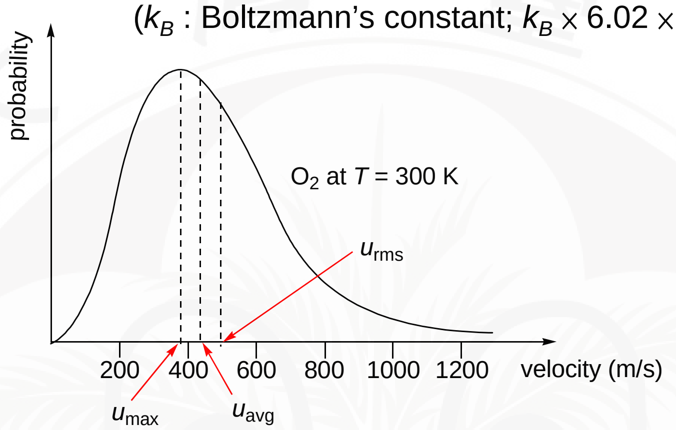
Distribution of u

described by Maxwell-Boltzmann distribution law

(1831-1879)   (1844-1906)

$$f(u) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} u^2 e^{-mu^2/2k_B T}$$

(k_B : Boltzmann's constant; $k_B \times 6.02 \times 10^{23} = R$)



$$u_{max} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$$

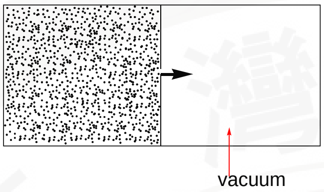
$$u_{avg} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

$$u_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

Qualitatively: u_{max}, u_{avg}, u_{rms} $\propto \sqrt{\frac{1}{M}}$

$M\uparrow$ $\quad\downarrow\quad\downarrow\quad\downarrow$

※ Effusion and diffusion



1846 Graham (1805 – 1869)
Two gases at the same *T*, *P*

Rate of effusion: $\frac{R_1}{R_2}=\frac{\sqrt{d_2}}{\sqrt{d_1}}$

From kinetic molecular theory:

$$\frac{R_1}{R_2}=\frac{u_{1avg}}{u_{2avg}}=\frac{\sqrt{8RT/\pi M_1}}{\sqrt{8RT/\pi M_2}}=\frac{\sqrt{M_2}}{\sqrt{M_1}}=\frac{\sqrt{d_2}}{\sqrt{d_1}}$$

1. A demonstration of the validity of the theory
2. Determine MW
3. Separation of gases

Similar for diffusion

Ex. Enrichment of $^{235}_{92}\mathrm{U}$ ($^{238}_{92}\mathrm{U}$)

↑

Natural abundance: 0.7%

UF_6: $$\frac{R_{235}}{R_{238}}=\frac{\sqrt{M_{238UF_6}}}{\sqrt{M_{235UF_6}}}=1.0043$$

Abundance: $$\frac{^{235}UF_6}{^{238}UF_6}=\frac{0.700}{99.3}=7.05\times10^{-3}$$

$(7.05 \times 10^{-3})(1.0043) = 7.08 \times 10^{-3}$

Enriched for one step

$$(\frac{0.700}{99.3})(1.0043)^{345}=\frac{3.00}{97.0}=30.9\times10^{-3}$$

※ Collisions of gas particles with the container wall

Collision frequency per sec.

$$Z \propto u_{\text{avg}} \times A \times \frac{N}{V}$$

$$\propto \sqrt{\frac{8RT}{\pi M}} \bullet \frac{AN}{V}$$

Actually
$$Z = \frac{1}{4}\frac{AN}{V}\sqrt{\frac{8RT}{\pi M}} = \frac{AN}{V}\sqrt{\frac{RT}{2\pi M}}$$

Ex. Impact rate of O_2 on 1.00 cm^2 at 1.00 atm, 27 ^{o}C?

Soln:

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.00\ \text{atm}}{(0.08206\ \frac{\text{L atm}}{\text{K mol}})(300\ \text{K})} = 4.06\times10^{-2}\ \frac{\text{mol}}{\text{L}}$$

$$\frac{N}{V} = 4.06\times10^{-2}\times6.02\times10^{23}\times1000 = 2.44\times10^{25}\ \frac{\text{molecule}}{\text{m}^3}$$

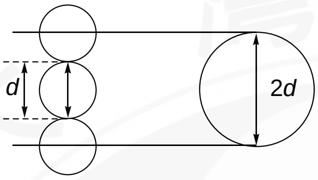
$$Z = (1.00\times10^{-4}\ \text{m}^2)(2.44\times10^{25}\ \text{m}^{-3})\sqrt{\frac{(8.3145\ \frac{\text{J}}{\text{K}\bullet\text{mol}})(300\ \text{K})}{2(3.14)(3.20\times10^{-2}\ \frac{\text{kg}}{\text{mol}})}}$$

$$= 2.72\times10^{23}\ \text{s}^{-1}$$

※ Intermolecular collisions

For ideal gas, not so important

Does not effect P, V, and T



Collision volume per second

$= \pi d^2 u_{avg}$

Number of collisions per second

$$= (\pi d^2 u_{avg})(\frac{N}{V}) = \pi d^2 \sqrt{\frac{8RT}{\pi M}}(\frac{N}{V}) = \frac{N}{V} d^2 \sqrt{\frac{8\pi RT}{M}}$$

Consider relative velocity ⇨ $(\sqrt{2})u_{avg}$

$$Z_{collision} = \sqrt{2}\frac{N}{V} d^2 \sqrt{\frac{8\pi RT}{M}} = 4\frac{N}{V} d^2 \sqrt{\frac{\pi RT}{M}}$$

For O_2 at 1.0 atm, 27 ^{o}C, assuming 300 pm diameter

$Z = 4 \times 10^9$ s^{-1}

Mean free path (λ)

The time between collision is $1/Z$

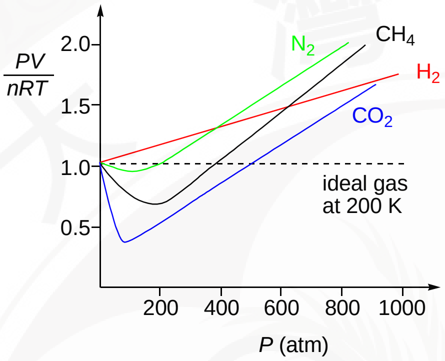
The distance between collision = $(1/Z)u_{avg} = \lambda$

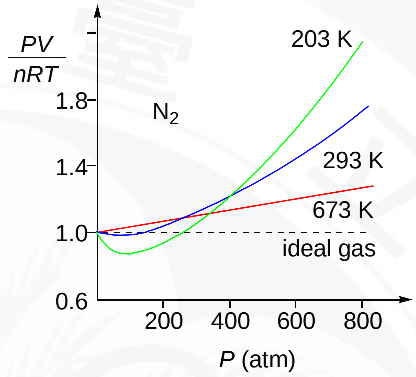
$$\lambda = \frac{\sqrt{\frac{8RT}{\pi M}}}{4\frac{N}{V} d^2 \sqrt{\frac{\pi RT}{M}}} = \frac{1}{\sqrt{2}(\frac{N}{V})(\pi d^2)}$$

$\lambda = 1 \times 10^{-7}$ m for O_2

※ Real gases

Ideal gas: $\frac{PV}{nRT} = 1$





Real gases approach ideal behavior at low *P* and high *T*

◎ Van der Waals' modification (1873)

$$V_{\text{ideal}} \rightarrow V_{\text{obs}} - nb$$

$$P_{\text{ideal}} \rightarrow P_{\text{obs}} + a\left(\frac{n}{V_{obs}}\right)^2$$

Concentration term

van der Walls' equation

$$\left[P_{obs} + a\left(\frac{n}{V_{obs}}\right)^2\right](V_{obs} - nb) = nRT$$

a, *b* determined by exp.

gas	*a* ($L^2 \cdot atm \cdot mol^{-2}$)	*b* ($L \cdot mol^{-1}$)
He	0.0341	0.0237
H_2	0.244	0.0266
O_2	1.36	0.0318
CH_4	2.25	0.0428
CO_2	3.59	0.0427

$$P_{obs} + \frac{an^2}{V_{obs}^2} = \frac{nRT}{V_{obs} - nb}$$

$$P_{obs} = \frac{nRT}{V_{obs} - nb} - \frac{an^2}{V_{obs}^2}$$

For 1 mol of gas

$$P_{obs} = \frac{RT}{V - b} - \frac{a}{V^2}$$ Cf. ideal gas $$P = \frac{RT}{V}$$

b increases *P*

volume factor

a decreases *P*

Intermolecular forces

Another view

$$[P_{obs} + a(\frac{n}{V_{obs}})^2](V_{obs} - nb) = nRT$$

⇨ $$\frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{RTV} = \underbrace{\frac{1}{1-\frac{b}{V}}} - \underbrace{\frac{a}{RTV}}$$ (for 1 mole)

At high *P*
→ *b* outweighs *a*
→ *PV/RT* > 1

At low *P*
→ *V* is large
→ *a* outweighs *b*
→ *PV/RT* < 1

At high *T* → *V* is large
Fast moving → interparticle interaction is relatively small

Overall
→ Approaching ideal
at high *T* and low *P* (higher *V*)

$$\frac{PV}{RT} = 1 + \frac{bP}{RT} - \frac{a}{RTV} + \frac{ab}{RTV^2}$$

※ Chemistry in the atmosphere

◎ Ozone in troposphere (對流層)

$NO_2(g) \xrightarrow{h\nu} NO(g) + O(g)$

From exhaust (also include NO)

$O(g) + O_2(g) \rightarrow O_3(g)$

ozone

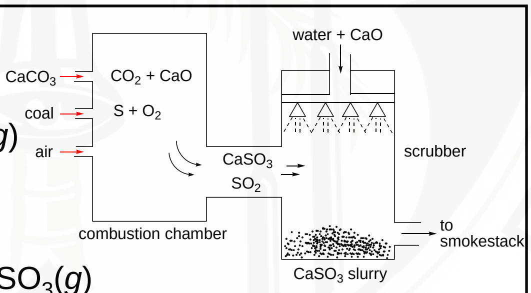
$NO(g) + \frac{1}{2} O_2(g) \rightarrow NO_2(g)$

Overall: $\frac{3}{2} O_2(g) \rightarrow O_3(g)$

↓

Other pollutants

◎ Coal burning



$S(s) + O_2(g) \rightarrow SO_2(g)$

In coal

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

Formation of acid rain

Exhaust treatment

Lime stone: $\underset{\text{powdered}}{CaCO_3(s)} \xrightarrow[\Delta]{} CaO(s) + CO_2(g)$

lime

$CaO(s) + SO_2(g) \rightarrow CaSO_3(s)\downarrow$

Calcium sulfite